Datamemo

Date: September 21, 2000

To: Barbara S. Larsen
DuPont Science and Engineering
Experimental Station, P.O. Box 80228
Wilmington, DE 19880-0228

From: Robert Bethem
ALTA Analytical Laboratory

Re: Development of an Analytical Procedure for the Analysis of PFOC and PFOS in Liquid Surfactants by LC-API/MS/MS

INTRODUCTION

A liquid chromatography atmospheric pressure ionization tandem mass spectrometry method (LC-API/MS/MS) was evaluated for the analysis of PFOC (FC-143) and PFOS (FC-95) with 3 product ion confirmation. A draft method (Alta method AMPFO1) is being provided along with this Datamemo. Although the method was initially developed and evaluated for the analysis of both PFOC and PFOS, the draft provided was optimized more specifically for PFOC.

The demonstrated range of reliable response for the method is 1 to 50 ppm. *The method has not been rigorously validated.* Experiments using standard additions to 3 different surfactants were conducted in order to evaluate the accuracy and feasibility of the analytical approach. The analytical raw data included with this report has been organized by analysis dates. A general description and summary of these results has been included with this report.

METHODOLOGY

The LC/MS/MS conditions developed for this method are routine and straightforward. The method was developed for 3 product ion confirmation and the instrument optimization was based on the least abundant product ion in contrast to a typical quantitative target analysis that would be optimized for the most abundant product ion. A simple reverses phase gradient was used for the separation.

The success of this method seems to hinge on the ability to dilute and inject the surfactant products with acceptable precision and accuracy. Using a mixture of 50/50 (v/v) water/methanol as a diluent yielded very nice linearity and accuracy for PFOS but inconsistent results for PFOC. Using 100% water as the diluent seems to work much better for PFOC but the linearity and accuracy for PFOS deteriorated. Since the initial sample screening (3/29/00) indicated that there were no detectable amounts of PFOS in the samples provided, the final analysis and standard additions experiments used 100% water as the diluent (6/8/00).

A second limiting factor of the method is the inability to demonstrate a clean solvent blank for PFOC. In fact, the LOQ is limited by the amount of background found in the blanks. Although the PFOC background can be controlled, the background levels range from between 2% and 30%. In nearly all cases, the blanks injected at the beginning of the injection sequence contained the highest background levels with subsequent blanks showing less background as the analytical sequence progressed. The need to set the LOQ higher due to the background combined with the need to detect 3 product ions for confirmation limits the overall dynamic range for the method dramatically. For the work described here, the demonstrated calibration range was only 1 – 50 ppm compared to a typical API/LC/MS/MS quantitative method based on 1 product ion with a dynamic range of 250 to 1000.

Results from 3 separate days of analysis are summarized on Tables 1 through 3.

SAMPLE DESCRIPTION AND RECEIPT

The following samples (product) were received in 1 shipment on 11/23/99 and logged into ALTA's sample control database (ALIS™) with unique sample identification numbers.

ALTA ID	Client Description
7709_0001	[redacted]
7709_0002	
7709_0003	

ORGANIZATION OF RAW DATA

The raw data provided has been organized into 4 folders. A description of the contents of these folders and the analyses conducted is summarized in the table below.

Folder	Date	Notebook	Description
PFOC – Spectra and Chro MD	1/28/00 – 3/28/00	Vol. 100 p. 1-6	Instrument tuning, optimization for 3 ions, chromatography development, initial evaluation and range finding for product.
PFOC – Alta 7709	3/29/00	Vol. 100 p. 7-9	Analysis of product. Datamemo dated April 4, 2000 describing analysis and summary of work conducted to date. 50/50 water/methanol uses as the diluent.
PFOC – Alta 7709	6/5/00	Vol. 100 p. 10-12	Analysis of product and standard additions using 50/'50 water/methanol. Standard addition to diluted product.
PFOC – Alta 7709	6/8/00	Vol. 100 p. 13-14	Analysis of product using 100 water as the diluent. Standard additions made directly to the product prior to dilution.

DISCUSSION OF RESULTS

1. Need to run extensive studies to understand the nature of the carryover and/or background levels found in blanks. Probably need to evaluate different sources of reagents. We have found that background and carryover can be controlled more effectively by running isocratic methods or starting the gradient at higher organic concentrations. This should be evaluated also.
2. If a PFOS analysis is needed along with PFOC, the linerarity, precision and accuracy should be evaluate using different diluents and dilution schemes.
3. Once above issues are studies more thoroughly, a more exhaustive method validation should be conducted to determine the limit of detection, quantitation, precision and accuracy of the method.

TABLE 1 - Results From 3/29/00

ALTA ID	ALTA Filename	Client Description	Dilution	PFOC (ppm)	PFOS (ppm)
7709_0001	032900A-010	[redacted]	1:1000	46	ND[1]
7709_0002	032900A-013		1:4000	168	ND[1]
7709_0003	032900A-016		1:1000	1.7	ND[1]

[1] Not Detected, The demonstrated limit of detection based on 3 ion confirmation is 1 ppm for samples diluted 1:1000. Based on the signal to noise for the primary ion only, the *estimated* limit of detection for PFOS is 0.1 ppm.

TABLE 2 - Results From 6/5/00,

ALTA ID	ALTA Filename	Client Description	Dilution	PFOC ppm)	STD Addition	Amt. Found	%Rec.
7709_0001	A000605112	[redacted]	1:5000	81	45.5	113	89%
7709_0002	A000605115		1:20,000	202	182	351	91%
7709_0003	A000605117		1:1000	2.8	0.91	2.2	59%

TABLE 3 - Results From 6/8/00,

ALTA ID	ALTA Filename	Client Description	Dilution	PFOC (ppm)	STD Addition	Amt. Found	%Rec.

7709_0001	A000608110	[redacted]	1:10,000	90.5	100	191	100%
7709_0002	A000608112		1:40,000	249	200	462	97%
7709_0003	A000608106		1:1000	1.6	2	3.8	95%